



Supporting Information

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69451 Weinheim, Germany

Probing the Charge Build-Up and Dissipation on Thin PMMA Film Surfaces at the Molecular Level by XPS**

*Eda Yilmaz, Hikmet Sezen, and Sefik Suzer**

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SUPPORTING INFORMATION

As also mentioned in the main text of the manuscript, we can estimate the MMA monomer density of the PMMA using the bulk density of 1.2 g/cm^3 ,^[1] to be $\sim 4 \times 10^{14} \text{ units/cm}^2$ on the surface, which reveals that approximately 1 out of 10^4 monomer units carries a surface charge. This also tells us that a monomer unit occupies an area of ca. $0.5 \times 0.5 \text{ nm}$. For the total of 10^4 monomer units we obtain an area of $50 \text{ nm} \times 50 \text{ nm}$ as shown in Figure S1 below.

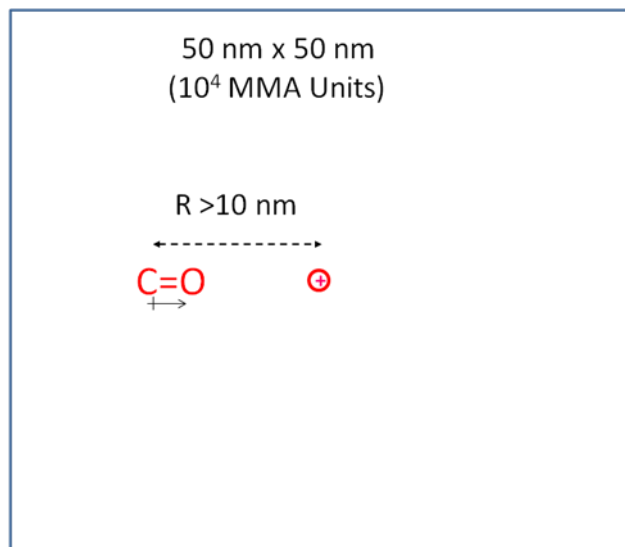


Figure S1. Schematic representation of the carbonyl dipole interacting with a point charge ca. 10 nm away.

For a simple ion-dipole interaction, by considering the carbonyl group having a dipole moment of $\sim 1 \text{ D}$ interacting with a unit charge $\sim 10 \text{ nm}$ away, the interaction energy can be estimated using the equation given below:^[2]

$$\Delta E = - \mu \cdot Q / (4\pi \epsilon_0 \epsilon R^2)$$

Where, R is the average distance between the dipole and the charge (taken as 10 nm), μ is the dipole moment (taken as $\sim 1 \text{ Debye}$), Q is the unit charge, and ϵ is the dielectric constant of the PMMA film (taken as ~ 2). This equation yields only 10^{-4} eV , too small compared to the observed energy of 0.07 eV .

[1] R. C. Weast, M. J. Astle, W. H. Beyer, *CRC Handbook of Chemistry and Physics*, 55th ed., CRC Press Boca Raton, FL, **1974**.

[2] J. Israelachvili, *Intermolecular and Surface Forces*, 2nd ed. Academic Press, London, **1991**.